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GALLIUM IN NUCLEAR REACTORS

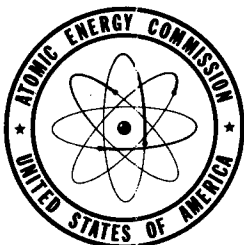Considerations for Use as a Primary Coolant

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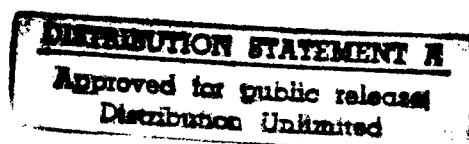E. A. Fromm
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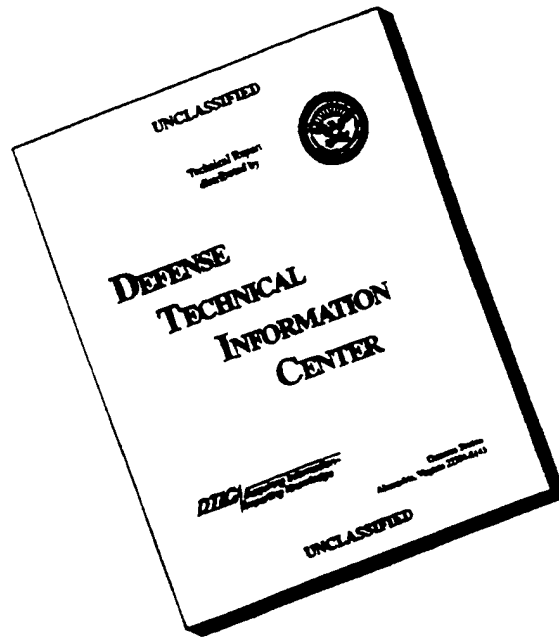
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FOREWORD

The unusual operating conditions of nuclear power reactors necessitate the use of unusual coolants. Thus, one desires a coolant which possess a low cross section for absorbing neutrons, good heat-transfer efficiency, a low melting point and a high boiling point. Furthermore, a material which can contain the coolant, at the desired temperature, with insignificant rates of corrosion, is needed.

The element gallium possesses some of the requisite properties. It is a unique material, having a very low melting point, and a very high boiling point. It melts at 30°C., and suitable alloying might be capable of lowering the melting point to below room temperature. The boiling point is high, about 2000°C. Being a liquid metal, the heat transfer characteristics would be good, though not so good as those of some other liquid metals.

The absorption cross section of gallium is rather high, 2.2 barns per atom. This is a severe handicap, but since the cross section might be reduced by proper alloying, and since good coolants need be present in the reactor in only relatively small amounts, one cannot rule out the use of gallium on account of its cross section alone. The availability of gallium is not high due in part to a lack of utility of the material. Nevertheless, a sufficient supply of gallium exists for this use.

Since gallium had some promise as a reactor coolant, owing to its unique properties, research on the subject was merited. Such research was begun at the request of the Bureau of Ships, U.S.N. The research had as its objectives, determining the effect of alloying on melting point and on cross section, and studying the corrosion of possible container materials by gallium.

In this research, no alloys were found which had a significantly lower melting point and simultaneously a significantly lower cross section. Neither was it found possible to reduce the melting point of certain otherwise suitable alloys considerably by small gallium additions, and thereby obtain a low melting point material with a low cross section.

The corrosion of possible container materials by gallium is high, in general. Of the metallic materials, only tungsten, a material which is exceedingly difficult to fabricate, and which itself has a high absorption cross section, appears to resist attack completely. Nonmetallic materials might be useable for corrosion resistance, but possess serious handicaps themselves, especially of heat transfer and radiation damage.

SUMMARY

In considering gallium as a primary liquid-metal heat-transfer medium for nuclear power plants, its relatively high thermal neutron-absorption cross section is offset to some extent by its low melting point. Further lowering of the melting point may be effected by alloying gallium with elements of lower thermal neutron-absorption cross section, and, at the same time, improve in small measure the over-all nuclear properties of the gallium alloy. Tin, zinc, and aluminum are the only elements with lower cross section than that of gallium, which also lower its melting point. The ternary Ga-Sn-Zn- eutectic alloy had advantages over the binary Ga-Sn and Ga-Zn eutectic alloys. The ternary Ga-Sn-Zn eutectic was found to contain 82Ga-12Sn-6Zn and melt at 17°C., better than the binary eutectics, 92Ga-8Sn melting at 20°C., and 95Ga-5Zn melting at 25°C.

To facilitate dilution of the Ga-Sn-Zn eutectic with more zinc so as to lower the gallium content with minimum raising of the melting point, the liquidus surface of the ternary system was determined. Dilution of the ternary

eutectic with 18Pb-82Sn alloy was also investigated for a few concentrations. The Pb-Sn dilution appears to be somewhat better than the zinc dilution, in that liquidus temperatures 10°-15°C. lower are obtained for alloys of a given gallium content. In all cases the solidus temperature is 17°C., and the diluted eutectic alloys are pasty at room temperature. Dilution of the Ga-Sn-Zn eutectic with Pb-Sn-Bi eutectic was found to be unfeasible, because the two eutectics appear to be immiscible.

Tungsten was found to be the most corrosion resistant of the available container metals for gallium at elevated temperature. No evidence of corrosion of tungsten was found after testing for times up to 96 hours at 1500°F. Tantalum was the next most corrosion-resistant metal found for gallium. Tantalum appeared to be satisfactory for service at 1000°F., but not at 1500°F. The growth of the Ga-Ta intermetallic compound on tantalum was found to be 0.0001 $\sqrt{t}$ inches at 1500°F. and 0.00001 $\sqrt{t}$ inches at 1000°F. (t expressed in hours). Molybdenum and titanium were found to be attacked too severely by gallium to be useful as container materials at 1000°F. and 1500°F. Beryllium was attacked intergranularly at 1500°F. and would be unsatisfactory as a container at that temperature. Indications were that it may be satisfactory at 1000°F. Molybdenum may be protected against attack by siliconizing. The siliconized coating is brittle, however, and siliconized molybdenum is not recommended as a container in preference to tungsten or tantalum. Siliconizing does not protect iron against attack by gallium.

The chief disadvantages of gallium as a primary coolant for nuclear reactors are its borderline thermal neutron cross section and its corrosivity to containers at elevated temperatures; the chief advantages of gallium are its low melting point, the further lowering of the melting points and gallium content by the use of Ga-Sn-Zn alloys, and the ability of tungsten to contain gallium at temperatures up to 1500°F. This latter advantage actually

may be classified as a disadvantage, since tungsten can be processed into forms other than rod and wire only with excessive difficulty, and is heavy, expensive, and has a high thermal neutron absorption cross section.

Weighing advantages against disadvantages, it has been concluded that gallium and gallium-rich alloys are unsuitable as primary coolants for nuclear reactors.

EXPERIMENTAL WORK

Low Melting Gallium Alloys

Experimental thermal analysis techniques used in this work are described in Appendix I.

General

As a first approximation, the development of low melting gallium alloys must be based on alloying elements which lower the melting point of gallium. For use as liquid metals in nuclear reactors of the thermal type, either as a primary heat-transfer medium or as a solvent for uranium, the alloy developed should not have a high thermal neutron capture cross section. Since the cross section of gallium is borderline, this means that alloying elements of higher cross section cannot be used.

The development of the lowest melting gallium alloy for primary reactor applications resolves itself into finding the eutectic temperature and composition of the complex system of gallium with all the elements which lower its melting point and which have smaller cross sections.

Possible Alloying Elements

Information from the literature, summarized in Table 1, indicates that tin, aluminum, and zinc were the only elements of lower thermal neutron

TABLE 1. AVAILABLE INFORMATION ON THE EFFECT OF BINARY ADDITIONS
ON THE MELTING POINT OF GALLIUM

Type of Effect	Metal	Gallium-Rich Eutectic		Reference
		% Addition	Temperature, °C.	
Melting Point Lowering				
Lower cross section than gallium	Tin	8	20	2
	Aluminum	Close to Ga	26	3
	Zinc	5	25	2
Higher cross section than gallium	Indium	25	16	4
	Silver	5	25	5
No Melting Point Lowering				
Lower cross section than gallium	Bismuth	0	30	2
	Lead	0	30	2
	Potassium	0	30	6
	Sodium	0	30	6
Higher cross section than gallium	Cadmium	0	30	2
	Mercury	0	30	2
	Copper	0	29	1
No Information	Arsenic			
	Calcium			
	Cerium			
	Magnesium			
	Antimony			
	Silicon			
	Thallium			

cross section than gallium that caused a lowering of the melting point of
gallium. Indium and silver also lower the melting point of gallium, but are
of little interest for use in the primary parts of a reactor because of their
high thermal-neutron cross sections. Of the elements known that do not lower
the melting of gallium, there is some ambiguity on the behavior of copper.
Weibke[1] obtained solidus arrest temperatures of 29°C. for Cu-Ga alloys from
60-97%Ga, 0.8°C. lower than the generally accepted melting point. This may
be the effect of a eutectic close to gallium, or, more probably, is the re-
sult of impurities in the gallium or experimental error.

The elements listed under the "no information" heading were of po-
tential interest if they lowered the melting point of gallium. Their effects
were determined experimentally for this reason. Binary alloys containing
nominally 2 per cent of each of these elements were prepared in the form of
2-gram melts by placing the components in a graphite crucible and holding in
an argon atmosphere at 370°C. for 5 hours. The melts were then subjected
to thermal analysis. In all cases, the solidus temperature found was 30°C.,
the melting point of gallium. These elements did not lower the melting point,
and were not considered further as components of a eutectic-type alloy.

Thus, the only elements of interest for the lowest melting gallium
alloy for primary reactor considerations were tin, aluminum, and zinc. Further
effects of these elements in combination are given in the next section.

Gallium-Tin-Zinc Alloys

Preliminary considerations of this system for low melting alloys
were encouraging. All three binary systems were of the simple eutectic type.
The composition and melting points of the eutectics were as follows: Sn-9Zn
(199°C.), Ga-8Sn (20°C.), and Ga-5Zn (25°C.). Therefore, the probability of
a ternary eutectic was high. For reasons to be discussed later, aluminum was

useless as an alloying constituent, leaving this system as the only one of interest for low-melting gallium-rich eutectic alloys of three or more components. Consequently, a considerable effort was expended in working out the liquidus surface.

By thermal-analysis methods (See Appendix I) it was quickly determined that the ternary eutectic temperature was 17°C., three degrees lower than the gallium-tin eutectic. The composition of the ternary eutectic was determined by following the eutectic valley lines issuing from the three binary eutectics as determined by thermal analysis of selected ternary alloys. The ternary eutectic composition found was 82Ga-12Sn-6Zn. Thus, the Ga-Sn-Zn ternary eutectic is a considerable improvement over the binary Ga-Sn eutectic; namely, 11% less gallium (82%Ga to 92%Ga) and 3°C. lower melting point (17°C. to 20°C.).

Compositions and thermal arrests of gallium-tin-zinc alloys are given in Table 2*. Data on the binary Ga-Sn and Ga-Zn systems were taken from Reference No. 2, and data on the binary Sn-Zn system from Reference No. 7. The liquidus surface obtained in the ternary system is shown in Figure 1, with an enlarged view of the gallium-rich corner in Figure 2. The field where primary gallium is crystallized is not known with precision, because enough alloys to determine it completely were not tested. The surface shown is accurate to ± 2-1/2°C., however. The eutectic line arrests obtained experimentally were checked against those expected from the liquidus surface. In all cases a good check was obtained.

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* Liquidus arrests were not obtained on Alloys No. 9 and No. 37. This may have been because of the smallness of the arrest or because of the cooling curve was not started from high enough temperature. Usually, in the field where primary tin crystallized, no eutectic line arrest was detected. The reason for this probably was because the eutectic line concerned (from the Ga-Sn binary eutectic to the Ga-Sn-Zn ternary eutectic) was so close in temperature to the ternary eutectic that on normal supercooling the eutectic line arrest was masked by the eutectic arrest.

TABLE 2. THERMAL ANALYSIS DATA ON Ga-Sn-Zn ALLOYS

| Alloy No.	Composition Weight, Per Cent			Liquidus, °C.	Thermal Arrests Eutectic Line, °C.	Solidus, °C.	Type of Curve Used
	Ga	Sn	Zn				
1	20	74.0	6.0	149	-	17	Inverse rate
2	20	72.0	8.0	147	--	17	Ditto
3	20	70.0	10.0	165	146	17	"
21	20	79.0	1.0	163	-	17	"
22	20	77.0	3.0	157	-	17	"
23	20	60.0	20.0	225	141	17	"
32	20	65.0	15.0	199	144	Not checked	"
4	40	55.0	5.0	115	-	Ditto	"
5	40	53.0	7.0	113	-	19	"
6	40	50.0	10.0	120-125?	111	17	"
24	40	59.0	1.0	122	-	Not checked	"
25	40	57.0	3.0	117	-	Ditto	"
29	40	45.0	15.0	163	106	"	"
31	40	47.5	12.5	148	107	"	"
18	50	34.0	16.0	157	85	17	"
19	50	28.0	22.0	182	76	Not checked	"
20	50	22.0	28.0	203	65	Ditto	"
7	60	36.0	4.0	80	-	"	"
8	60	33.0	7.0	77	-	17	"
9	60	30.0	10.0	-	72	Not checked	"
26	60	39.5	0.5	87	-	Ditto	"
27	60	38.0	2.0	84	-	"	"
28	60	25.0	15.0	141	62	16	"
30	60	27.5	12.5	125	64	Not checked	"
10	80	17.0	3.0	32	-	18	"
11	80	14.0	6.0	26	21	17	"
12	80	11.0	9.0	84	-	Not checked	"
33	80	7.5	12.5	110	19	16	I-R and time-temp.
34	80	4.0	16.0	123	21	16	Ditto
37	85	13.0	2.0	-	18	17	Time-temp.
35	86	4.0	10.0	54?	22	17	Ditto
38	86	8.0	6.0	19.5	-	17	"
13	90	8.0	2.0	19	-	17	"
14	90	5.0	5.0	23	-	17	"
36	90	4.0	6.0	22	-	16.5	"
15	92	2.0	6.0	27	-	17	"
16	94	4.0	2.0	27	-	17	"
17	95	2.0	3.0	24	-	17	"
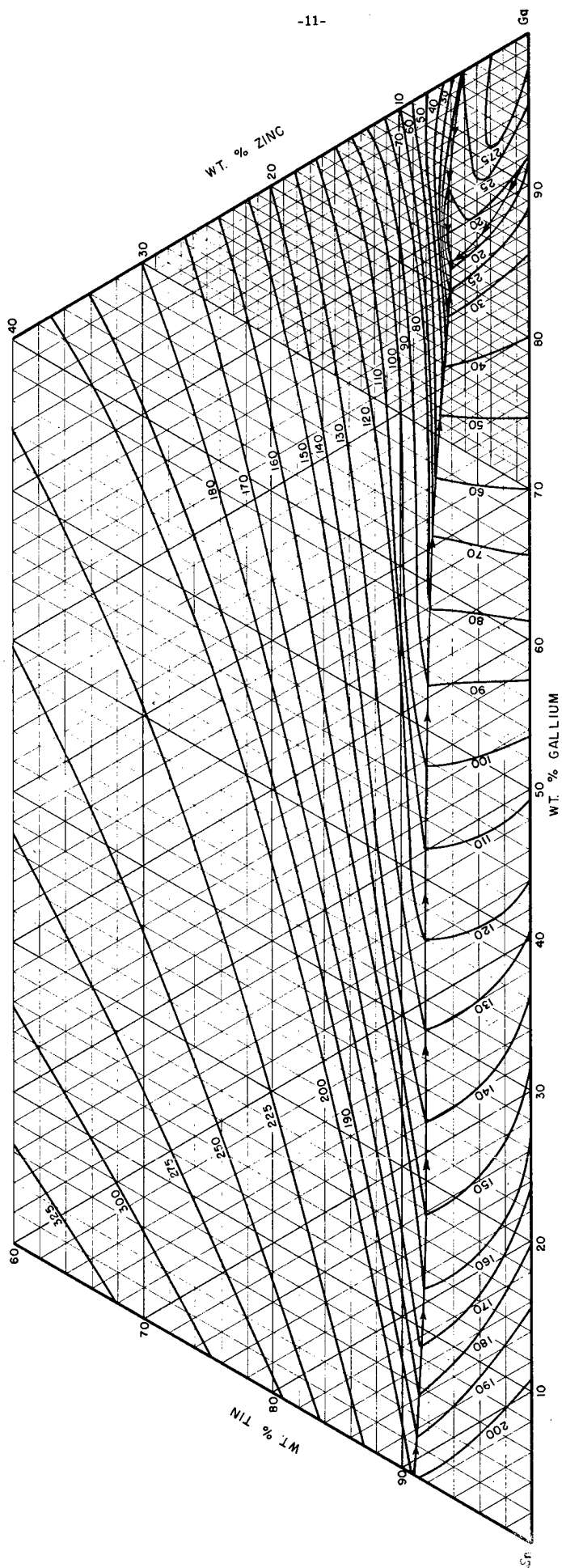
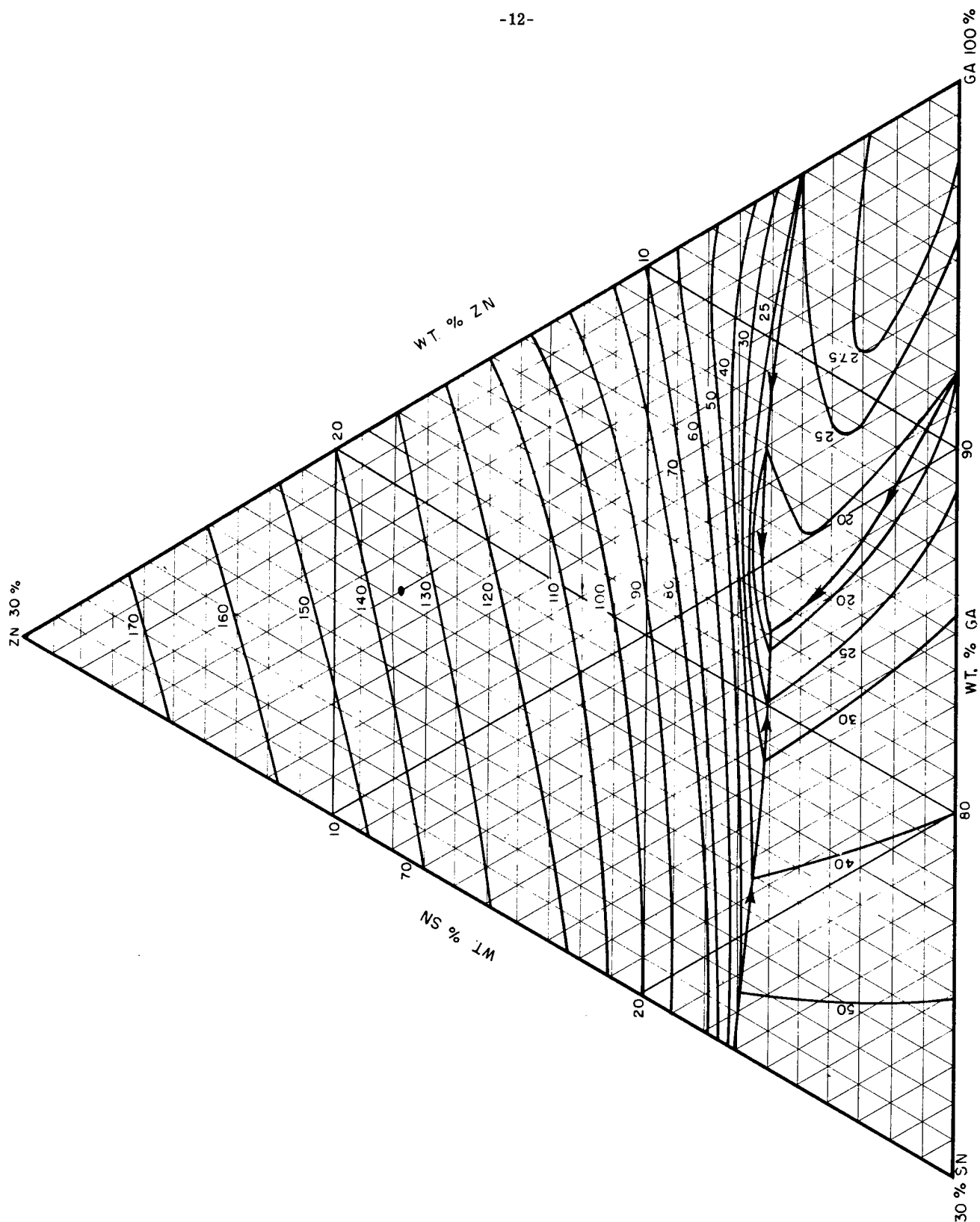FIGURE 1. LIQUIDUS SURFACE OF Ga-Sn-Zn SYSTEM.

FIGURE 2. LIQUIDUS SURFACE OF GALLIUM CORNER GA-SN-ZN SYSTEM

Several attempts were made to determine the ternary eutectic composition by filtering a partially molten alloy at the ternary eutectic temperature. An alloy of 85Ga-13Sn-2Zn weighing 16 grams was made up. It was cooled until eutectic supercooling had taken place, and solidification started. The partially solidified alloy at 17°C., the eutectic temperature, was then filtered through a sintered quartz filter. The filtrate weighed 11 grams, and analysed 86.4Ga-11.8Sn-2.0Zn. This obviously does not agree with the eutectic composition obtained from thermal analysis data. The ternary freezing diagram in Figure 1 permits an explanation for the discrepancy: the eutectic line arrest was supercooled, and, when the filtration was made, the liquid of the eutectic line composition was filtered. The eutectic line composition, when all primary tin had crystallized, would be 87.5Ga-10.5Sn-2Zn. Since the actual filtrate is halfway between this composition and the original melt, it appears that about half the primary tin got through the filter also. From this and similar experiences, it was concluded that filtration to isolate eutectic liquids is unreliable.

In consideration of low-melting alloys of Ga-Sn-Zn for liquid metal use, it would be better practice to choose compositions on the Ga-Sn side of the eutectic valley because of the high slope of the liquidus surface of the primary zinc field. Much better control of liquidus temperature would be possible, since small variations in composition would have little effect on melting point. This would preclude use of alloys containing more than about 6.0% zinc for liquid metal applications.

Alloys Containing Aluminum

Aluminum added to Ga-Sn-Zn alloys at first appeared to be advantageous. The invariant point of gallium-rich Ga-Sn-Zn-Al alloys on a virgin run was found to be 15.5°C. However, on rerunning the same alloy, the invariant point obtained was 17°C., identical with the Ga-Sn-Zn eutectic.

The Ga-Sn-Zn-Al alloys were found to oxidize very rapidly in air at room temperature. Held at 50°C. for from 3 to 4 hours, they tended to turn to powder. To see which of the elements was promoting the oxidation, the alloys listed below were held in air at 100°C. for 24 hours and the following observations were made:

Alloys			Observations
80Ga	20Sn		Some skin, not serious
97.5Ga	2.5Zn		Heavy skin, not serious
97.5Ga	2.5Al		Heavy skin, reforms on removal in air
78Ga	20Sn	2Zn	Some skin, not serious
78Ga	20Sn	2Al	Very bad oxidation, little liquid left

It is apparent that aluminum is responsible for the bad drossing of Ga-Sn-Zn-Al alloys. Drossing by the aluminum appears to be worse when tin is present. The observation noted before, that the quaternary eutectic arrest reverts to the Ga-Sn-Zn arrest, is the result of loss of the aluminum by oxidation.

No further work was done with aluminum. This left the Ga-Sn-Zn eutectic as the only possible ternary or higher eutectic alloy for primary use in reactors.

Dilution of Ga-Sn-Zn Eutectic

Zinc. The Ga-Sn-Zn eutectic may be diluted to lower gallium contents with minimum increase in temperature by following the eutectic valley line in the Ga-Sn-Zn system to the Ga-Zn binary eutectic. The alloys are sandy or gritty at room temperature, and do not tend to form large lumps.

Lead-Tin. Only limited data are available on this dilution. Data obtained on dilution of Ga-Sn-Zn eutectic with 82Sn-18Pb are given below:

Ga-Sn-Zn Eutectic, %	Pb-Sn, %	Overall %				Liquidus, °C.	Solidus, °C.
		Ga	Sn	Zn .	Pb		
0	100	0	82.0	0	18	205	183
18	82	14.8	69.1	1.1	15	146	17
39	61	32.0	54.7	2.3	11	117	17
100	0	82.0	12.0	6.0	0	17	17

The solidified alloys at room temperature were sandy or gritty, similar to the eutectic diluted with zinc.

Lead-Tin-Bismuth. Dilution of the Ga-Sn-Zn eutectic with the Pb-Sn-Bi eutectic was made at several gallium contents with the results listed as follows:

Ga-Sn-Zn Eutectic, %	Pb-Sn-Bi Eutectic, %	Over-all Composition, %					Liquidus, °C.	Solidus, °C.
		Ga	Sn	Zn	Pb	Bi		
0	100	0	16.0	0	32.0	52.0	95	95
5	95	4.1	15.8	0.3	30.5	49.3	89	0
25	75	20.5	15.0	1.5	24.0	37.0	90	22
50	50	41.0	14.0	3.0	16.0	26.0	94	20
75	25	61.5	13.0	4.5	8.0	13.0	96	21
100	0	82.0	12.0	6.0	0	0	17	17

The liquidus of the Ga-Sn-Zn eutectic is raised sharply to the Pb-Sn-Bi eutectic temperature by the addition of Pb-Sn-Bi eutectic. The solidus of the gallium alloy is raised only slightly by the addition of Pb-Sn-Bi eutectic.

These are practically the conditions for two immiscible liquids, each of which freezes at its own melting point. Or, if the liquids are miscible above the Pb-Sn-Bi eutectic melting point, it is clear that the Pb-Sn-Bi eutectic component of the alloy all freezes out at its melting point. There appears to be a slight interaction between the two alloys, because the solidus temperature of Ga-Sn-Zn is raised slightly.

Comparison of Diluents. Figure 3 shows the liquidus curves obtained with the three diluents. The zinc and the lead-tin diluents have normal increases in liquidus temperature as the gallium content decreases. Also, they form true, pasty solid-liquid mixtures on cooling to room temperature. The lead-tin-bismuth diluent results in a freezing curve characteristic of immiscible liquids, and crystallizes as a solid lump in the liquid gallium alloy on cooling. The best diluents then are lead-tin and zinc. Lead-tin is preferred, because its liquidus curve is 10-15°C. lower than zinc. Additional work on variation of the lead-tin ratio of the diluent would bring further lowering of the liquidus temperature. The optimum would be reached when the eutectic valley to the Pb-Sn binary eutectic was located.

Corrosion of Metals by Gallium

Experimental techniques used in evaluating corrosion resistance are given in Appendix II, Corrosion Testing, Equipment and Methods.

General

After a study of the preliminary results reported by Wilkinson[8, 9, 10, 11] on the corrosion of container materials by gallium, it was decided that there were only four metals which showed promise. These metals, tantalum, tungsten, beryllium, and molybdenum were chosen then for further investigation.

Titanium was included in the corrosion tests, because in previous work high
purity iodide titanium was not used. Molybdenum coated with silicon and sili-
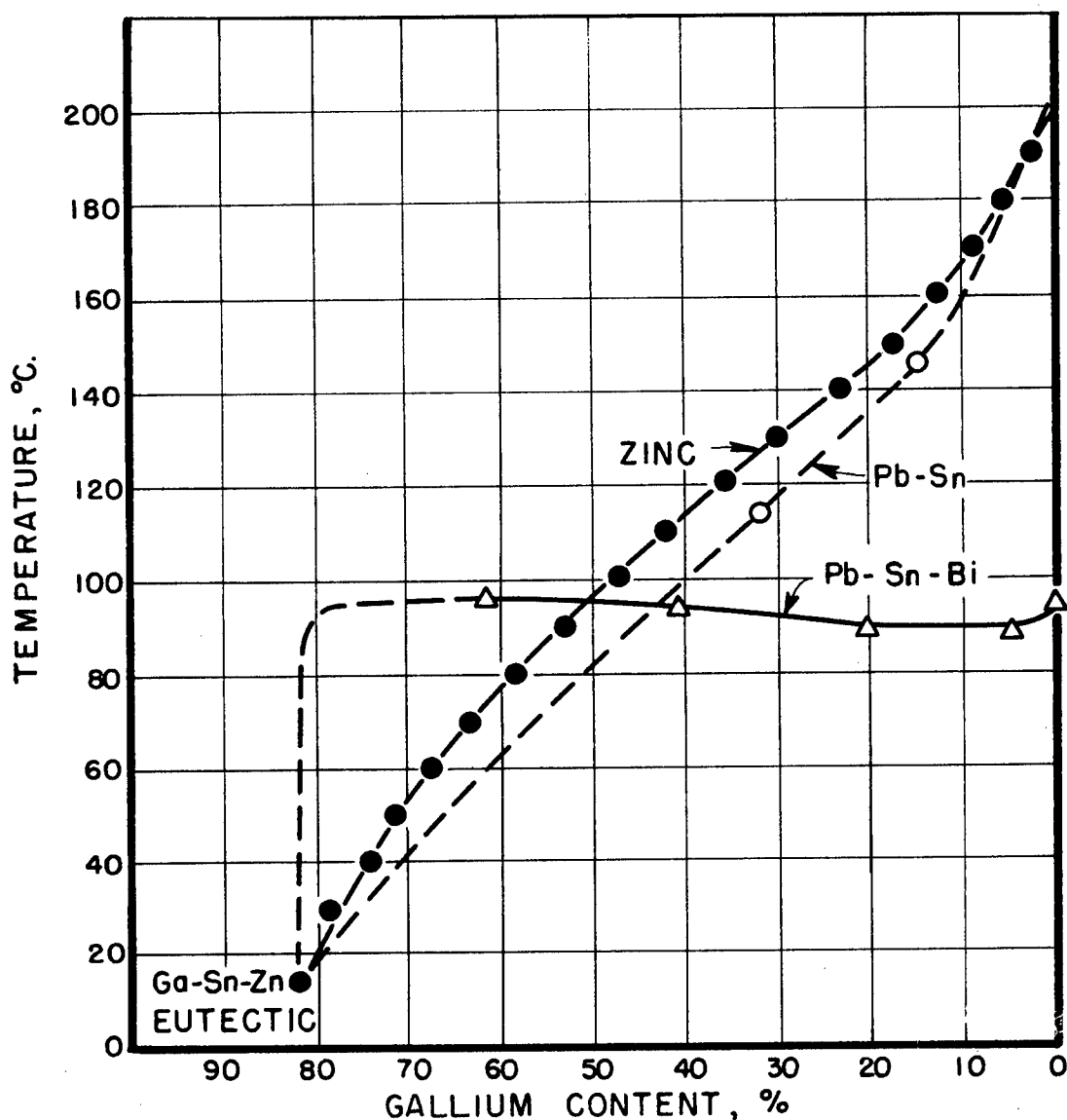conized iron were later added as other possibilities.

FIGURE 3. DILUTION OF Ga-Sn-Zn EUTECTIC WITH
ZINC, Pb-Sn(18 % Pb), AND Pb-Sn-Bi
EUTECTIC. CURVES SHOW LIQUIDUS
TEMPERATURE ONLY. ALL SOLIDUS
TEMPERATURES IN RANGE 17-22 °C.

The initial plans for corrosion evaluation were to establish a corrosion rate by analysing the gallium for metal pickup. However, because of the type of reaction encountered, this was found to be not so important as a metallographic examination of the metal specimen after corrosion in gallium. Apparently because the liquid solubility of the metals in gallium was very small at testing temperatures, most of the apparent reaction came from formation of intermetallic phases adhering to the test specimen. Pure gallium was used as the corrodent in all except one check case. The results would not be expected to be greatly different with gallium than with gallium-rich alloys.

Results of tests run at 1500°F. and 1000°F. are given in Table 3. A series of tests at 750°F. is not included, because it was made before the technique of obtaining wetting was perfected (see Appendix II), and, therefore, are not reliable.

Tungsten

Tungsten was found to be resistant to attack by gallium at temperatures up to 1500°F. Although tungsten could be wet by gallium, no evidence of alloy layer formation or decrease in thickness of tungsten specimens could be detected after immersion in gallium for up to 96 hours at 1500°F.

Figure 4 shows a micrograph of a tungsten specimen after corrosion testing. Alloy layers, which usually show up in unetched sections, are not apparent in the micrograph. Etching the specimen did not reveal any evidence of attack. The cracks present were formed during mounting for metallographic examination, and are the result of the characteristic brittleness of tungsten. No additional embrittlement of the tungsten is believed to have been incurred as a result of corrosion.

TABLE 3. SUMMARY OF DATA ON CORROSION OF METALS BY GALLIUM

Specimen	Diameter, in.	Weight, g.	Length of Test, hrs.	Temp., °F.	Wetted	Metal Pickup by Gallium, % (Spectro. Anal.)	Final Diam. Unreacted Metal, in.	Thickness Outer Reaction Layer, in.	Thickness Inner Reaction Layer, in.	Comments
Ta 5	0.080	0.3782	12	1500	Yes	< 0.05	0.079	0.0004	—	No visible reaction
Ta 10	0.080	0.3429	24	1500	No	< 0.05	0.078	0.0006	—	No visible reaction; specimen appeared dirty
Ta 11	0.080	0.3460	48	1500	Yes	ca 1.0	0.077	0.0008	—	Appears to have reacted slightly
Ta 12	0.080	0.3220	96	1500	Yes	ca 0.5	0.077	0.0009	—	No visible reaction
Ta 13	0.080	0.3468	96	1000	Yes	Not checked	0.080	0.0001	—	No visible reaction
Ta 11a	0.080	0.3311	48	1500	Yes	Not checked	0.078	0.0004	—	Slight reaction apparent (Ga-Sn-Zn alloy rather than pure Ga)
Mo 9	0.080	0.2085	24	1500	Yes	1-5	0.068	0.0052	0.0029	Appears to have reacted
Mo 10	0.080	Not weighed	48	1500	Partially	1-5	—	0.0400	—	Appears to have reacted; duplex alloy throughout
Mo 11	0.080	0.2053	96	1500	Yes	1-5	—	—	—	Appears almost completely reacted
Mo 12	0.080	0.2103	32	1500	Yes	1-5	0.030	0.0035	0.0037	Appears to have reacted; duplex alloy except for slight core
Mo 13	0.080	0.2102	96	1500	Yes	1-5	0.079	See comment	See comment	Appears to have reacted; duplex alloy throughout
Mo 14	0.080	0.2096	96	1000	Yes	Not checked	—	—	—	Appears almost completely reacted
Ti 7	0.080	0.0919	24	1500	Yes	0.5-2.0	0.060	0.0024	0.0014	Partially reacted
Ti 8	0.080	0.0856	72	1500	Yes	0.5-2.0	0.064	0.0042	0.0014	Appears to have reacted
Ti 9	0.080	0.0850	96	1000	Yes	Not checked	—	—	—	Completely reacted
W 2	0.080	0.4079	50	1500	Yes	0.001-0.005	0.083	None	—	No visible reaction
W 3	0.080	0.4083	96	1500	Yes	0.003-0.008	0.080	None	—	No visible reaction
W 4	0.080	0.4081	96	1000	Yes	Not checked	0.080	None	—	No visible reaction
Mo-Si 1	0.088	0.2438	24	1500	No	No <.001; Si present	0.080	None	—	No visible reaction
Mo-Si 2	0.088	0.2432	96	1000	No	Not checked	0.080	None	—	No visible reaction
Be 1	0.080	0.0378	12	1500	Yes	Not checked	0.061	0.0025	—	Appears to have reacted; capsule brown-black inside
Be 2	0.079	0.0359	25	1500	Yes	Ditto	0.061	0.0033	—	Appears to have reacted; capsule brown-black inside
Be 3	0.079	0.0380	48	1500	Yes	"	0.055	0.0050	—	Reacted; capsule brown-black inside
Be 4	0.080	0.0360	96	1500	Yes	"	0.038	0.0083	—	Reacted; capsule brown-black inside
Be 5	0.080	0.0359	96	1000	Yes	"	0.076	None	—	No visible reaction

As a further indication of the resistance of tungsten to attack by gallium, tungsten rods were subsequently used to stir gallium alloys in thermal analysis experiments starting from temperatures as high as 2000°F. These rods did not appear to be attacked, even under these severe conditions, although no quantitative measurements were made.

Tungsten is judged to be a satisfactory metallic container material for gallium. Its limitations as a container for gallium come from other known characteristics of tungsten—like scarcity, difficulty of fabrication, poor weldability, etc.— not lack of corrosion resistance.
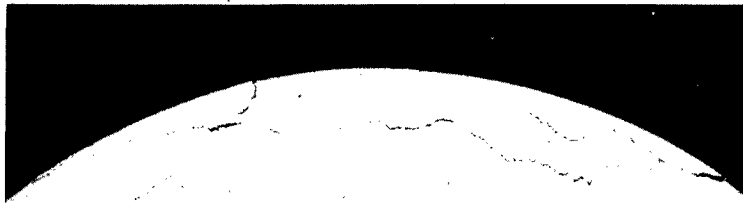
250X   Unetched   —   63935

Figure 4. Micrograph of tungsten rod after immersion in gallium for 48 hours at 1500°F. (Cracks shown were formed during sectioning, and are not evidence of corrosion attack.)

Tantalum

When wet by gallium, tantalum shows attack at both 1000°F. and 1500°F.,
as may be seen in the micrograph in Figure 5. The alloy layer formation at
1000°F. is about one-tenth that at 1500°F.; in 96 hours at 1000°F., the alloy
layer thickness was 0.0001 inch; for the same time at 1500°F. it was 0.001-inch
thick. The alloy layer thickness increases with time. It is not linear, how-
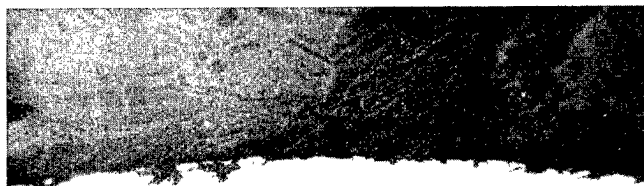ever. The thickness-time data and the calculated constants for the equation

$$x = k \sqrt{t}$$

which applies to this type of diffusion are shown in the following tabulation.
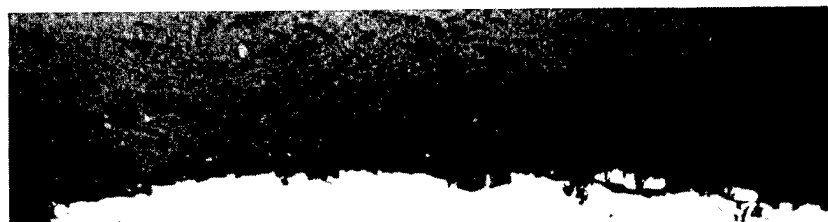
250X   63608

96 Hours at 1500°F.

250X   63952

96 Hours at 1000°F.

Figure 5. Micrographs of tantalum rods after immer-
sion in gallium for 96 hours at 1500°F.
and 1000°F. Unetched condition.

Temperature, °F.	t, time, hrs.	x, thickness, in.	$k = \frac{x}{\sqrt{t}}$ in./√hr.
1500	12	0.0004	0.00012
Ditto	24	0.0006	0.00012
"	48	0.0008	0.00012
"	96	0.0009	0.00009
1000	96	0.0001	0.00001

Thus, for corrosion of tantalum by gallium, the following equations appear to apply:

$$1500°F.: \quad x = 0.0001 \sqrt{t}$$

$$1000°F.: \quad x = 0.00001 \sqrt{t}$$

where x is thickness of alloy layer in inches, t is corrosion time in hours.

Corrosion of tantalum by Ga-Sn-Zn eutectic alloy is about half as severe as by gallium (cf. thickness of alloy layer after 48 hours at 1500°F., Spec. Ta-11 and Ta-11a). The constant of the equation, $x = k \sqrt{t}$, is $k = \frac{0.0004}{\sqrt{48}} = 0.00006.$

The corrosion (e.g., formation of alloy layer) of tantalum by gallium and Ga-Sn-Zn eutectic may be calculated for various times at 1500°F. and 1000°F. given below:

Temperature, °F.	Corrosion in Inches					
	Gallium			Ga-Sn-Zn		
	1 Mo.	6 Mo.	1 Yr.	1 Mo.	6 Mo.	1 Yr.
1500	0.0027	0.0066	0.0094	0.0016	0.0040	0.0056
1000	0.0003	0.0007	0.0009	–	–	–

From this, one may conclude that for service in liquid gallium at 1000°F. tantalum would be satisfactory. At 1500°F. the corrosion rate is borderline, and tantalum would not be satisfactory. The same conclusions would apply to corrosion of tantalum by Ga-Sn-Zn eutectic.

Molybdenum

Corrosion of molybdenum by gallium is severe at 1500°F. and 1000°F. Heavy intermetallic compound layers are formed (cf. Figure 6), and considerable molybdenum goes into the gallium by solution and by breaking off of the brittle compound formed. In some cases of prolonged exposure, intrusion of the Ga-Mo compound into the molybdenum in radial directions, such as is shown in Figure 7, was noted. This radial intrusion sometimes led to disintegration of the specimen.

Siliconized Molybdenum

Molybdenum may be protected against gallium attack by providing it with a coating of molybdenum silicide. The silicide-coated molybdenum is not met by gallium and is not attacked at either 1500°F. or 1000°F. This would be a satisfactory method of protection were it not for the brittle nature of the silicide coating. In a few places on the siliconized specimen, the coating was not perfect, and evidence of corrosion under the cracks was seen.

Titanium

Titanium was severely attacked by gallium at 1500°F. and 1000°F., as may be seen for a representative case in Figure 8. Two intermetallic compound layers were formed on the titanium specimens. The high pickup of titanium in the gallium noted in Table 3 undoubtedly is caused by flaking off of the brittle outer compound.

Beryllium

At 1500°F. gallium attack on beryllium was severe. The attack was intergranular, and entire grains broke away from the beryllium surface. This made the beryllium surface irregular and the cross section no longer round
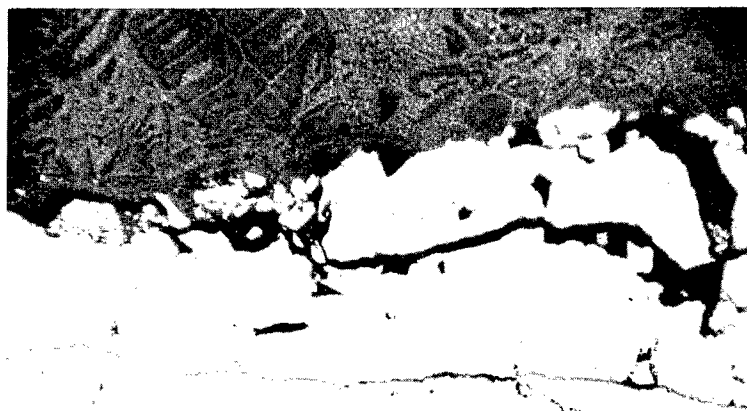
250X   Unetched   63606

Figure 6. Micrograph of molybdenum rod after immersion in gallium for 24 hours at 1500°F.

75X   Unetched   63609

Figure 7. Micrograph of molybdenum rod after immersion in gallium for 48 hours at 1500°F.

(cf. Figure 9). At 1000°F. the intergranular attack of the surface is not apparent from microscopic examination. That is, the surface area does not etch preferentially to the core as it does after exposure to gallium at 1500°F. However, there were areas on the 1000°F. specimen where grains were pulled from the surface. It is not known whether this was caused by mechanical means acting on the brittle beryllium, or by corrosion attack.

Siliconized Iron

Because of the success of siliconizing in protecting molybdenum against attack by gallium, some samples of siliconized iron were tested at 1500°F. They were completely disintegrated after 32 hours.

250X   Unetched   63603

Figure 8. Micrograph of titanium rod after immer-
sion in gallium for 24 hours at 1500°F.
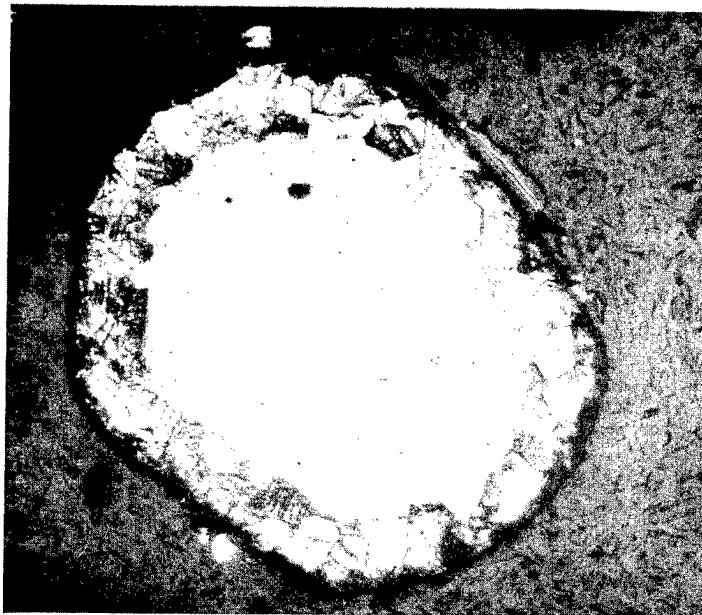
50X   64083

Figure 9. Micrograph of beryllium after im-
           mersion in gallium for 96 hours
           at 1500°F. Etched with dilute
           HNO_3-HF.

APPENDIX I

Materials Used

Gallium

In all cases, the gallium used came from the Eagle-Picher Company. Two lots of gallium were used in the course of the work. Analyses of the lots furnished by Eagle-Picher showed 0.0005% lead and 0.0050% copper. The first lot was considerably cleaner than the second lot, which had a mossy appearance as received. On melting the second lot, a scum formed on top and was skimmed off.

Results of warm vacuum-extraction experiments at 500°C. on the second lot were as follows:

| Sample | Condition | Hydrogen | |
		P.P.M.	Relative Volumes
Lot 2-768-900	Skimmed	2.5	0.16
Lot 2-768-900	Scum	40.0	2.7

No significant volume of other gases was obtained in these tests. The two lots of gallium behaved slightly differently as shown in the follow-ing thermal analyses:

Material Tested	Lot 2-639-900 (First Lot)	Lot 2-768-900 (Second Lot)
Pure Ga, melting point, °C.	29.8 (start), 30.2 (end)	27.2 (start), 30.3 (end)
80Ga-20Sn, eutectic temp., °C.	20.3 (start), 21.5 (end)	19.4 (start), 20.5 (end)
80Ga-20Sn, liquidus temp., °C.	36.4	36.3
Ga-Sn-Zn, eutectic temp., °C.	16.6 (start), 17.0 (finish)	15.3 (start), 16.7 (finish)

Spectrographic analyses of the two lots failed to show any metallic impurities in the second lot that would account for the invarient temperature lowering of approximately 1°C. The lowering may have been caused by the dissolved gallium hydride noted in the warm vacuum-extraction experiments. The gallium of the second lot used in thermal analysis work was melted and skimmed, and contained dissolved hydrogen to the extent of 2.5 P.P.M. For corrosion testing, all of the gallium used was degassed in vacuum.

Other Materials

In thermal analysis work, the following addition metals were used: Metal and Thermit Company high-purity tin, Bakers C. P. stick zinc, 99.996% aluminum (French high purity), and electrolytic lead (National Lead Company). The metals used for corrosion testing were: swaged tungsten rod (Fansteel), tantalum rod (Fansteel), molybdenum rod (Fansteel), iodide titanium rod (prepared at Battelle), extruded and rolled beryllium (regular grade), siliconized molybdenum (prepared at Battelle), and siliconized iron (prepared at Battelle).

APPENDIX II

Thermal Analysis, Equipment, and Methods

A method was developed for low-temperature thermal analysis in the temperature range, -72° to 250°C., which may be of more than current interest. The method was sensitive enough that with a specimen of only 2 grams of gallium, a freezing arrest of 30 minutes could be observed. For complex alloys, primary crystallization and eutectic line arrests of small magnitude could in general be detected.

No new principles were involved in the thermal analysis technique used. The Rosenbain temperature gradient furnace[12], adapted for low-temperature use, was the basis of the method. The gradient was set up in a stainless-steel tube, and the specimen was lowered through it at a constant rate while time-temperature or inverse rate data were taken. Careful control of the top and bottom temperatures of the gradient and good heat transfer from the walls to the specimen were essential to the success of the method, especially when it was desired to obtain liquidus arrests of small magnitude. In order to obtain good heat transfer, it was necessary to fill the entire tube and surround the specimen with oil.

A photograph of the thermal analysis equipment is shown in Figure 10, and a diagrammatic sketch in Figure 11. The furnace tube was made from a 2 inch round stainless-steel shaft, 16.5 inches long. A 0.75-inch hole was bored from the top to within 0.25 inch of the bottom, the top three inches were wound with eight feet of 18 gage Chromel A heating wire and the bottom three inches were finned to promote cooling. The whole tube except for the finned bottom was
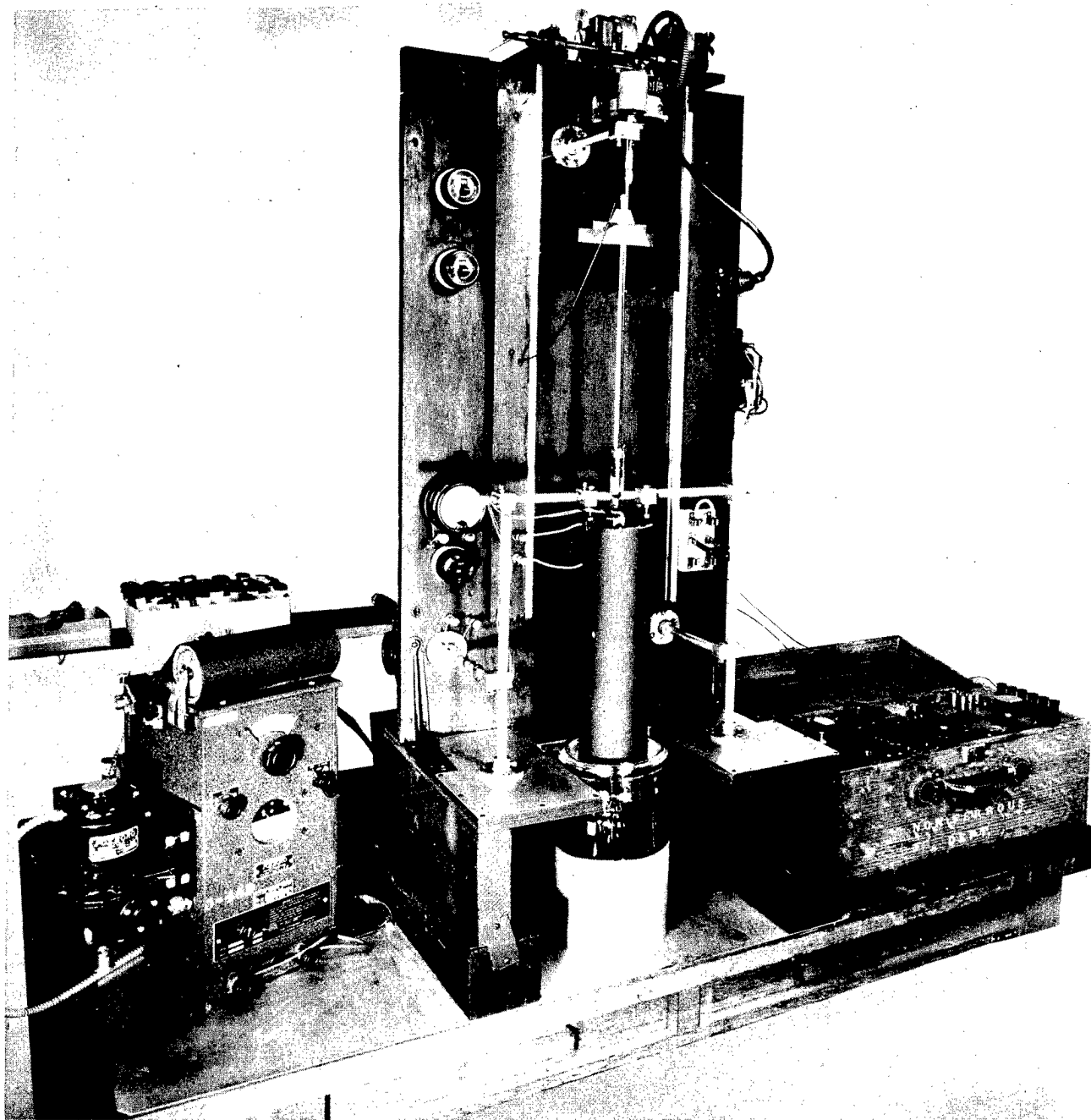
63848

Figure 10. Thermal analysis furnace and auxiliary equipment.
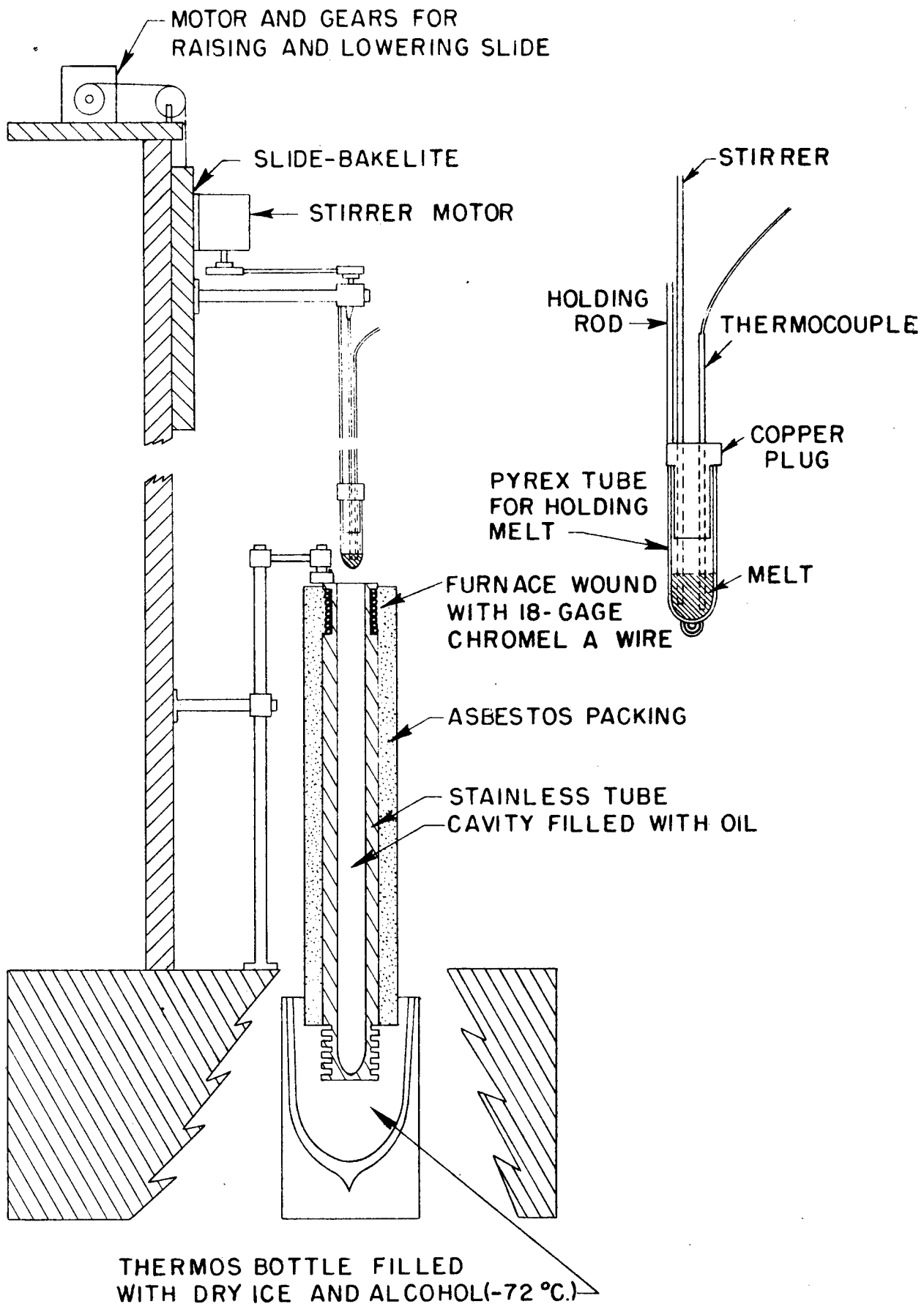
FIGURE 11. DETAIL OF THERMAL-ANALYSIS EQUIPMENT.

insulated with one inch of natural asbestos. The finned-bottom section was held in an equilibrium mixture of dry ice and alcohol at -72°C. and the top section heated to varying temperatures up to about 250°C.,depending on the maximum temperature desired for a particular alloy.

Two-gram melts were prepared under an oil cover in a graphite crucible, and then transferred to either a rubber finger cot for low-melting liquids or a glass thimble for the higher-melting liquids. The thimble or cot was then hung on the lowering device, the thermocouple and stirrer inserted in preparation for lowering the melt through the temperature gradient. To provide good thermal contact and prevent difficulty with air currents, the furnace cavity and the thimble were completely filled with a low pour-point synthetic oil.

To insure uniform temperature distribution throughout the melt, a small stirrer having a combined rotary and vertical motion was used. This stirrer rotating at six r.p.m. with a two-cycle vertical amplitude of 1/8 inch was found to give sufficient agitation.

Bare 28-gage copper-constantan thermocouples were used with the melt serving as the hot junction. For each melt, new ends of the wire were presented to overcome possible thermocouple contamination. All thermocouples were calibrated against ice and water for 0°C. and boiling water for 100°C.

All curves were taken using a Leeds and Northrup semiprecision potentiometer. Inverse rate curve readings were taken at intervals of 0.05 m.v. or 1.25°C. Time-temperature readings were taken usually at intervals of 30 seconds. The results were considered accurate to 0.5°C.

The rate of lowering through the temperature gradient varied from 1°C. per minute to 2.5°C. per minute, depending on the top temperature used.

Using the above-described furnace and holding setup, and exercising close control over the temperature gradient, very satisfactory curves were ob-

tained. Typical curves for gallium-rich alloys are shown in Figures 12 and 13.

Good liquidus arrests could be obtained during cooling, and, if a wide enough range existed between the liquidus and solidus, intermediate eutectic line arrests would be obtained. The eutectic component of the alloy usually supercooled so that eutectic or solidus arrests on cooling were not reliable. Heating curves were used to determine solidus temperatures. Conversely, heating curves were unreliable for liquidus arrests. In most cases, on alloys containing more than 80 percent gallium, it was necessary to use time-temperature heating curves for reliable data. This was because the liquidus and solidus were near to each other, and it was found that in such cases supercooling of the liquidus as well as the solidus occurred.
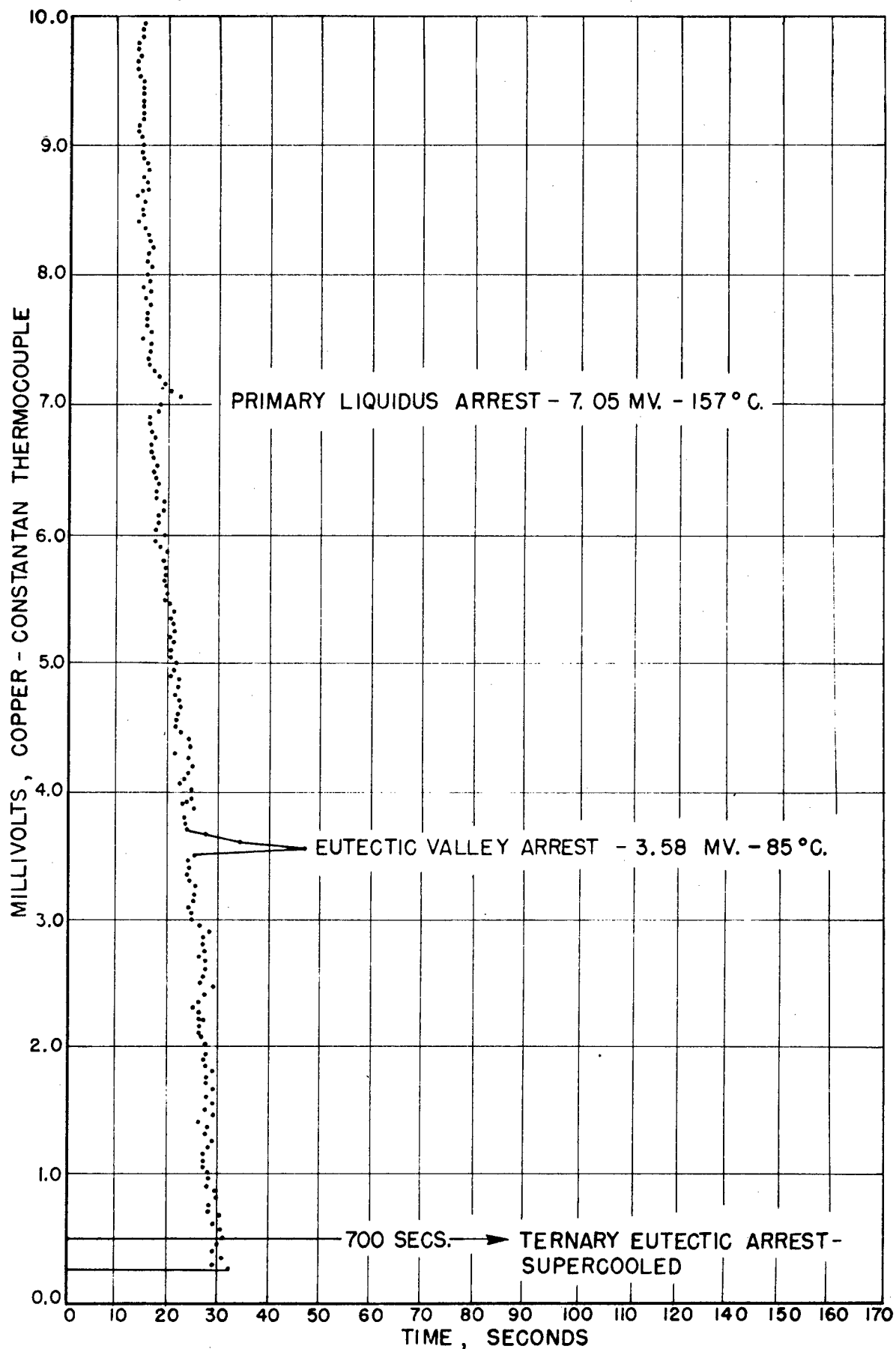
FIGURE 12. TYPICAL INVERSE RATE CURVE OBTAINED.
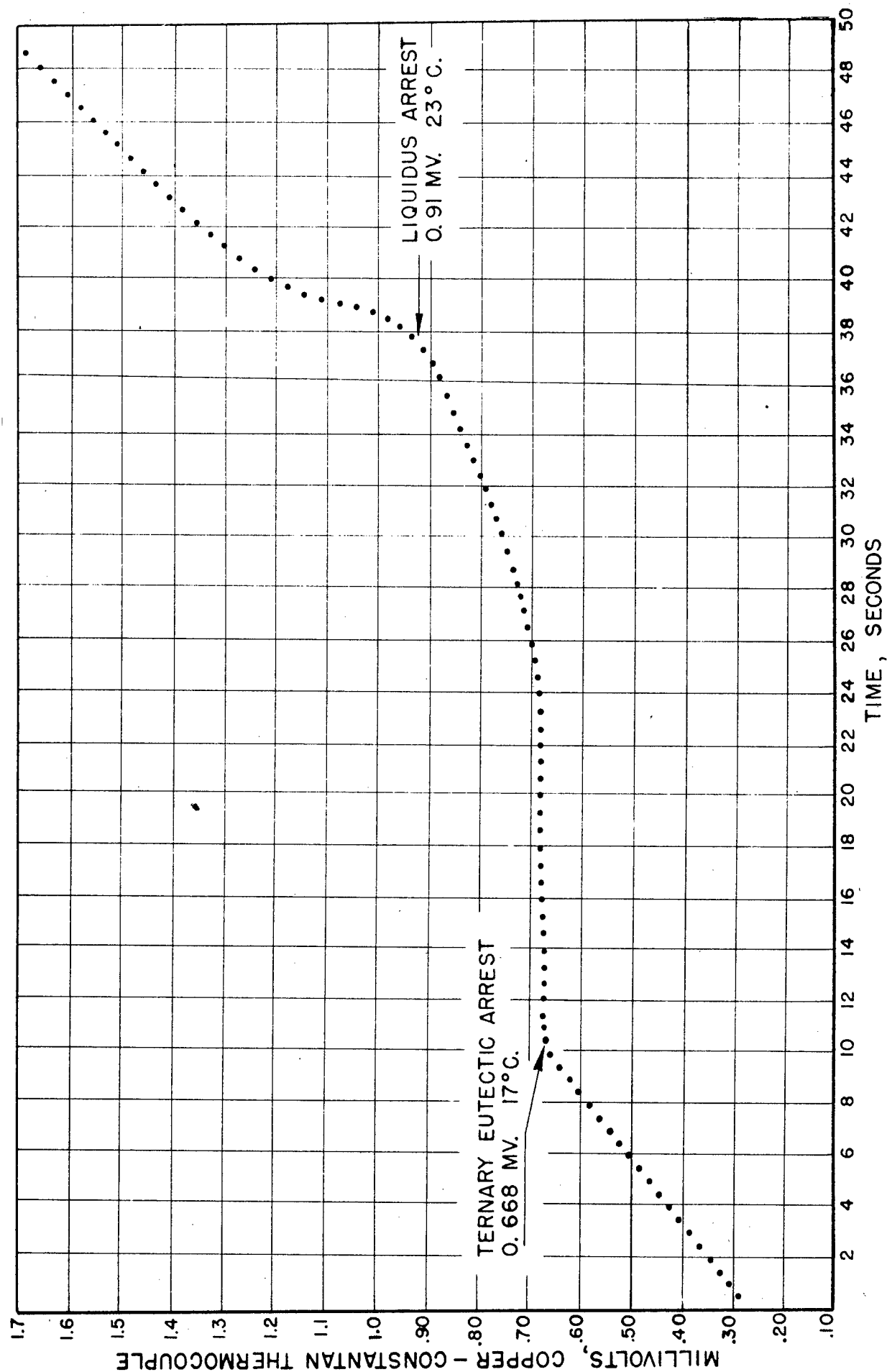ALLOY NO. 18, 50 GA. – 34 Sn – 16 Zn. COOLING.

FIGURE 13. TYPICAL TIME-TEMPERATURE CURVE OBTAINED. ALLOY NO. 14 90 Ga - 5 Sn-5Zn. HEATING.

APPENDIX III

## Corrosion Testing, Equipment, and Methods

The ideal test for corrosion by a liquid-metal-heat transfer medium should embody a moving liquid and a temperature differential. For gallium, a test setup employing both of these features would be costly, because of the large amount of gallium required. The test used had the liquid in motion, but had no temperature differential.

It was desirable to make the corrosion test as severe as possible under the temperature and time conditions used. The specimens to be corroded were first degreased, cleaned, and vacuum annealed to insure a fresh surface available for corrosion. Also, special precautions were taken to insure wetting of the specimen by the gallium.

Five grams of gallium and the specimens to be corroded were sealed in an evacuated capsule, and subjected to a tumbling motion at test temperature for standard lengths of time. The corrosion specimen was 0.080 inch in diameter and 0.250 inch long, and the capsule was of Vycor, 0.25 inch inside diameter by 2 inches long. Tumbling of the capsule was done at 6 r.p.m. on an axis perpendicular to the length of the ends 12 times per minute.

If the gallium is not degassed in vacuum before use, it blackens on heating in the capsule, and does not wet metals readily. To illustrate this effect, two capsules were prepared, one with degassed gallium and the other with as-received gallium. They were held at 1500°F. for 24 hours. Figure 14 shows the capsules after this treatment. The capsule with as-received gallium has become blackened on the sides, and the surface of the gallium itself has also

became blackened. The capsule with degassed gallium has remained unchanged, however. The blackening is believed to be evidence of gallium hydride. Hydrogen was found to be present in the as-received gallium to the extent of 0.16 relative volumes. When this gallium was sealed in the evacuated Vycor tube and heated, the dissolved hydrogen was released. On cooling, this hydrogen re-reacted with the gallium forming black gallium hydride on the walls of the capsule and on the surface of the gallium.
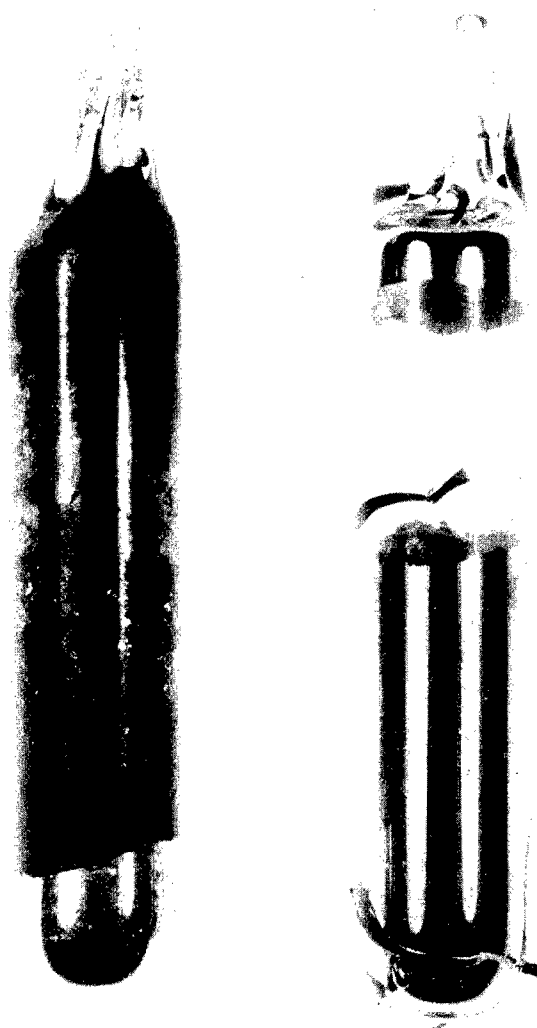
2X   62476

Figure 14.   Effect of degassing gallium before vacuum
             sealing in corrosion capsule. Capsule on
             right was degassed; capsule on left was not.
             Capsules held 26 hours at 1500°F.

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